

## Gelified IPN system as Polymer Electrolyte for Lithium Batteries

S. Passerini<sup>a</sup>, M. Lisi<sup>a</sup>, P. Villano<sup>a</sup>, F. Alessandrini<sup>a</sup>, T. Momma<sup>b</sup>, H. Ito<sup>b</sup>, T. Osaka<sup>b</sup>

<sup>a</sup> ENEA, C.R. Casaccia, Via Anguillarese 301, 00060 Rome, Italy

<sup>b</sup> Kagami Memorial Lab. for Materials Science and Technology; Dept. of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan

In this work we report on the realization and characterization of lithium batteries based on a gelified IPN (Interpenetrated Polymer Network) as electrolyte. Such blends are characterized by a co-continuous morphology consisting of two three-dimensionally interpenetrated polymer networks simply formed by hot-mixing two non-miscible polymers (1). Polymer blends have been already considered as base materials for the synthesis of gel electrolytes (2,3) but no particular investigations were devoted to the optimization of their microscopic morphology. Mixing immiscible polymers in the molten state, results in the formation of materials characterized by heterogeneous microstructures, which strongly affect the properties of the polymer blend itself. Example of microstructures that can be formed are droplet/matrix, fibrous, lamellar, and, of most interest, co-continuous (IPN) microstructures. In Figure 1 is shown a SEM image of the IPN developed in this work prepared by hot-mixing polystyrene and polyethyleneoxide in a 52:48 ratio by weight. The image, taken from a sample in which the PEO phase was etched with water, clearly show the continuous and three-dimensional network of polystyrene interpenetrated by a continuous and three-dimensional network of pores originally filled by the PEO phase.

The intrinsic advantage of IPN's consists in the possibility of selecting one of the polymers to impart mechanical stability and a second polymer to enable ionic conductivity via formation of a gel, which contains the electrolytic solution. The feasibility of using gelified IPN's as  $\text{Li}^+$ -ion conductor has already been proved in our previous work (4,5). A gelified polystyrene (PS)-polyethyleneoxide (PEO) IPN, which PEO phase was gelified with a 1M solution of  $\text{LiClO}_4$  in propylene carbonate-ethylene carbonate (1:1 by volume), has shown an ionic conductivity approaching  $10^{-3} \text{ Scm}^{-1}$  at room temperature. The ability to transport ions depends on the content of the electrolytic solution gelled in the IPN (see Figure 2). The ionic conductivity of the gelled IPN increases from  $2 \cdot 10^{-5} \text{ Scm}^{-1}$  up to  $0.8 \cdot 10^{-3} \text{ Scm}^{-1}$  for the weight fraction of electrolytic solution changing from 19% to 50%. Above such a content of solution the conductivity remains almost constant around  $10^{-3} \text{ Scm}^{-1}$ .

The ability of gelled IPN's to act as ionic conductor in a lithium battery as been tested by assembling electrochemical cells with a lithium anode and several composite cathodes containing *high-voltage* ( $\text{LiCoO}_2$ ,  $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ ) and *low-voltage* ( $\text{LiFePO}_4$  and  $\text{V}_2\text{O}_5$ ) active materials. Due to the presence of PEO in the electrolyte, the cells made with *high-voltage* cathodes showed a parasitic oxidative process taking place at about 3.8 Volts. Cells assembled with *low-voltage* cathodes showed much better performance. Figure 3 shows a typical discharge curve of a cell containing  $\text{LiFePO}_4$  discharged at C/20 rate at room temperature.

Summarizing, gelled IPN's appear very promising for the realization of gel-electrolyte lithium batteries. The concept of combining two immiscible polymers, one

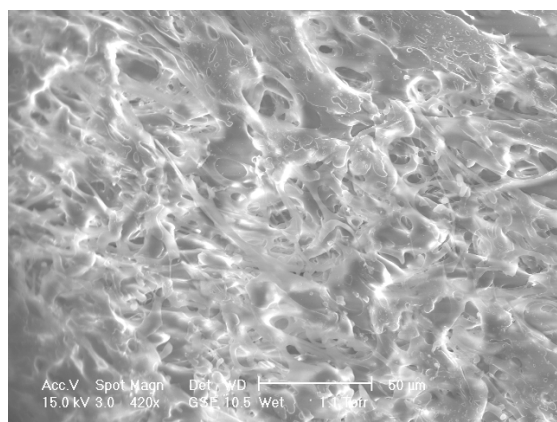
granting the mechanical stability and the second one the ionic conductivity via previous gellation with an appropriate electrolytic solution, has been proved successful for the synthesis of low-cost, environmentally friendly (no solvents and polluting procedures are needed to synthesize the IPN) gel-polymer electrolytes.

## Acknowledgements

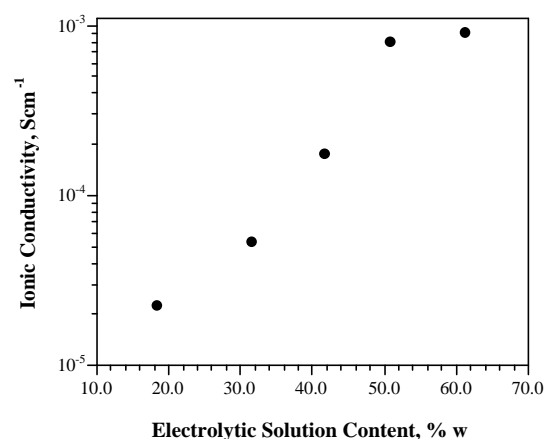
The groups at ENEA and Waseda would like to thank the financial support of MURST and NEDO (International Joint Research Grant "Advanced Li Battery Science"), respectively.

## References

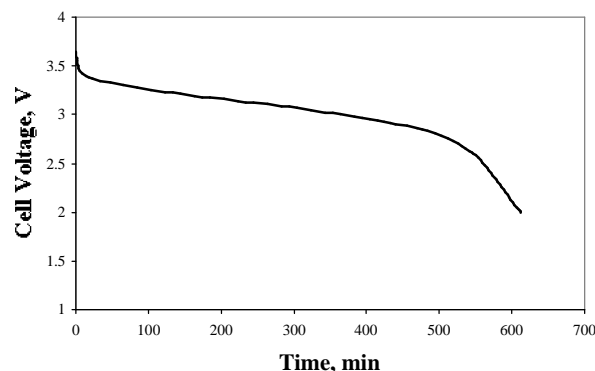
1. R.C. Willemse, A. Posthuma de Boer, J. Van Dam, and A.D. Gotsis, *Polymer*, **39**, 5879 (1998).
2. M. Oliver, US Patent 5,658,685 (1997).
3. W. Wieczorek, J. Stevens, *J. Phys Chem.*, **B101**, 1529 (1997).
4. F. Alessandrini, S. Passerini, It. Patent 2000A000683 (2000).
5. S. Passerini, F. Alessandrini, T. Momma, H. Otha, H. Ito, T. Osaka, *ESSL*, submitted for publication (2000).



**Figure 1.** SEM image of a PS-PEO (52:48w) IPN sample. The PEO phase was etched by dipping the sample in water.



**Figure 2.** Room temperature (25°C) conductivity of a gelled PS-PEO (52:48) IPN as a function of the electrolytic solution (1M  $\text{LiClO}_4$  in PC:EC, 1:1 by volume) content.



**Figure 3.** Typical discharge behavior of a Li/ 1M  $\text{LiPF}_6$ -EC:DMC (1:1w) in PS-PEO (52:48w) /  $\text{LiFePO}_4$  cell at R.T..